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54 Synthesis of a crystalline silicoaluminophosphate.

57 A method for the synthesis of the silicoaluminophosphate SAPO-37 comprises preparing a two-phase reaction mixture containing the required starting materials divided between a liquid organic phase and a liquid aqueous phase. The reaction mixture is then heated at a rate of from 5°C to 200°C per hour to a temperature of from 80°C to 200°, while being agitated in a manner sufficient to intimately admix the liquid organic and aqueous phases. Once nucleation of the silicoaluminophosphate occurs the agitated reaction mixture is heated at rate of from 5°C to 200°C per hour to a temperature of from 100°C to 300° and maintained then at the higher temperature and at a pH of from 2 to 9 until crystals of the desired silicoaluminophosphate are formed.

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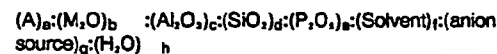
SYNTHESIS OF A CRYSTALLINE SILICOALUMINOPHOSPHATE

This invention relates to an improved method for preparing the crystalline silicoaluminophosphate SAPO-37, whereby synthesis is facilitated and the product exhibits high purity and catalytic utility.

Silicoaluminophosphate SAPO-37 and its conventional method of preparation are taught by U.S. Patent 4,440,871. SAPO-37 has a faujasite-type structure.

According to the present invention, there is provided a method for synthesizing a crystalline material comprising silicon, phosphorus and aluminum and exhibiting a characteristic X-ray diffraction pattern as shown in Table I of the specification which comprises:

a) preparing a reaction mixture comprising a liquid organic phase and a liquid aqueous phase, said reaction mixture comprising water, sources of aluminum oxide, silicon oxide, phosphorus oxide, an organic directing agent A, inorganic cations M and anions, and a substantially water-immiscible organic solvent, the components of said reaction mixture having the following relationship:



wherein a, b, c, d, e, f, g and h are numbers satisfying the following relationship:

$$a/(c+d+e) \text{ is less than } 4,$$

$$b/(c+d+e) \text{ is less than } 2$$

$$d/(c+e) \text{ is less than } 2,$$

$$f/(c+d+e) \text{ is from } 0.1 \text{ to } 15,$$

$$g/(c+d+e) \text{ is less than } 2, \text{ and}$$

$$h/(c+d+e) \text{ is from } 3 \text{ to } 150,$$

10 wherein upon initial preparation of said reaction mixture the source of one of the aluminum, silicon or phosphorus oxides is dispersed or dissolved in said organic phase;

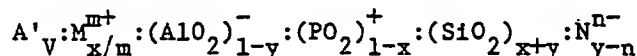
15 b) heating said reaction mixture at a rate of from 5°C to 200°C per hour to a temperature of from 80°C to 200°C;

c) agitating said reaction mixture in a manner sufficient to intimately admix said liquid organic and aqueous phases with each other;

20 d) when nucleation of said crystalline material occurs, heating said agitated reaction mixture at a rate of from 5°C to 200°C per hour to a temperature of from 100°C to 300°C;

25 e) maintaining said agitated reaction mixture at a temperature of from 100°C to 300°C and a pH of from 2 to 9 until crystals of said crystalline material are formed; and

30 f) recovering from said reaction mixture said crystalline material characterized by a composition, in the anhydrous state, as follows:



wherein A' represents the total of organic directing agent A plus organic solvent, v is the number of moles of A', m is the valence of cation M, n is the valence of anion N, and x and y are numbers of from greater than -1 to less than +1 which satisfy the relationship:

(1) if x is 0, then y is not 0,

(2) if y is 0, then x is not 0,

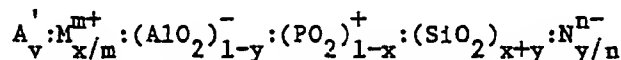
(3) the sum of x + y is greater than 0 and less than 1,

said crystalline material having an ion exchange capacity of

40 at least about 0.05 meq/g.

45 The improved method of this invention provides an increase in yield of about 200% over the SAPO-37 preparation method taught in U.S. Patent 4,440,871. It also offers a reproducible method for making SAPO-37 with higher cation exchange capacity for identical silicon content and a higher number of total cation exchange sites.

50 The crystalline material produced by this method is characterized by a composition in which the number of atoms of aluminum and phosphorus is greater than the number of atoms of silicon, i.e. Al + P greater than Si. As synthesized, the characteristic composition for such material, in the anhydrous state, is as follows:



wherein v is moles of A' which is the occluded organic material resulting from organic directing agent A and/or organic solvent used in the synthesis of and filling micro-porous voids of the silicoaluminophosphate, which material may be removed upon calcination; M is an inorganic cation of valence m; N is an anion of valence n; and x and y are numbers of from greater than -1 to less than +1 which

60 satisfy the relationships:

(1) if x is 0, then y is not 0,

65 (2) if y is 0, then x is not 0,

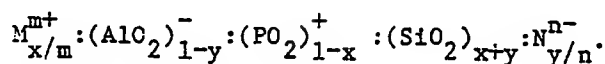
(3) the sum of x + y is less than 1, but greater than 0,

e.g., from 0.02 to 0.99.

In the above composition, when x is greater than y, the silicoaluminophosphate is a cation exchanger with potential use as an acidic catalyst. When x is less than y, the silicoaluminophosphate is an anion exchanger with potential use as a basic catalyst. In any event, the

silicoaluminophosphate will exhibit an ion exchange capacity of at least about 0.05 meq/g (higher than that of conventional SAPO-37 with identical framework composition prepared as taught in U.S. Patent 4,440,871), making it attractive for use as a catalyst support.

The composition of the silicoaluminophosphate in the anhydrous state with organic material removed, and with M, m, N, n, x and y as above-defined, is as follows:



The SAPO-37 prepared hereby is a molecular sieve and possesses a definite distinguishing crystalline structure which exhibits a characteristic X-ray powder diffraction pattern as detailed in Table 1.

TABLE 1

Interplanar d-Spacing (A)	Relative Intensity
14.25 ± 0.2	vs
8.65 ± 0.1	m
7.45 ± 0.1	w
5.65 ± 0.05	m-s
4.75 ± 0.05	m-s
4.35 ± 0.05	m
4.20 ± 0.05	w
3.90 ± 0.03	w
3.77 ± 0.03	s
3.46 ± 0.03	w
3.30 ± 0.02	m
3.02 ± 0.02	w
2.91 ± 0.02	w
2.85 ± 0.02	m
2.76 ± 0.02	w
2.63 ± 0.02	w

These X-ray diffraction data were collected with a Rigaku X-ray system, using copper K-alpha radiation. The positions of the peaks, expressed in degrees 2 theta, where theta is the Bragg angle, were determined by step-scanning at 0.02 degrees of 2 theta intervals and a counting time of 1 second for each step. The interplanar spaces, d, measured in Angstrom units (A), and the relative intensities of the lines, I/I_s, where I_s is one-hundredth of the intensity of the strongest line, including subtraction of the background,

were derived with the use of a profile fitting routine. The relative intensities are given in terms of the symbols vs = very strong (75-100%), s = strong (50-74%), m = medium (25-49%) and w = weak (0-24%). It should be understood that this X-ray diffraction pattern is characteristic of all the species of SAPO-37 compositions synthesized by the present invention. Ion exchange of cations with other ions results in a silicoaluminophosphate which reveals substantially the same X-ray diffraction pattern with some minor

shifts in interplanar spacing and variations in relative intensity. Other variations can occur, depending on the silicon/aluminum and phosphorus/aluminum ratios of the particular sample, as well as its degree of thermal treatment.

If synthesized with an aluminum/phosphorus atomic ratio of greater than one, the crystalline silicoaluminophosphate will exhibit an aluminum/silicon atomic ratio of greater than 1.5, and usually in the range of from 1.6 to 600. When the aluminum/phosphorus ratio is of less than one, the phosphorus/silicon atomic ratio of the silicophosphoaluminate is greater than unity, usually within the range of from 1.2 to 600.

The present method uses a two-phase synthesis reaction mixture, which enables the retention in solution in the organic phase one or more of the reactants which are normally insoluble or unstable in the aqueous phase under the synthesis conditions. Such a procedure enables the preparation of improved SAPO-37 product when compared to conventional synthesis. The two-phase synthesis method also enhances the ability to control the crystallization reaction. In addition to its templating role, the organic directing agent can also act as a surfactant. It can help the codispersion of the organic and aqueous phases containing the reagents.

In the synthesis method of the present invention, the reaction mixture contains sources of silicon oxide, phosphorus oxide and aluminum oxide, an directing agent and an organic solvent in the relationship hereinbefore set forth.

The organic directing agent is a mixture of two different organic cations, a tetrapropylammonium cation and a tetramethylammonium cation. The ratio of tetrapropylammonium cations/tetramethylammonium cations in the mixture will be from 10/1 to 80/1. The compounds providing these cations may be halides, e.g., chloride or iodide, hydroxides, acetates, sulfates, carboxylates, or combinations thereof. Tetrapropylammonium cations alone direct synthesis of an ALPO-5 type structure, whereas tetramethylammonium cations alone direct synthesis of a sodalite type structure. Using a mixture of these cations, SAPO-37 is the directed crystal product structure.

The useful sources of aluminum oxide include any known form of aluminum oxide or hydroxide, organic or inorganic salt or compound.

The useful sources of phosphorus oxide include any known form of phosphorus acids or phosphorus oxides, phosphates and phosphites, and organic derivatives of phosphorus.

The useful sources of silicon oxide include any known form of silicic acid or silicon dioxide, alkoxy- or other compounds of silicon.

The organic solvent used to form the two-phase reaction mixture can be any organic liquid which is substantially immiscible with water under the crystallization conditions of the present method. Non-limiting examples of such a solvent include the C_1 - C_{12} alcohols, phenols, and naphthols; and other substantially water-immiscible organic solvents. Polar organic compounds are preferred for the organic phase solvent.

The inorganic cations and anions essentially present in the reaction mixture are generally not provided by separately added components. Rather, these cations and anions will frequently come from compounds added to the reaction mixture to provide the other essential components such as the silicon, alumina and/or phosphorus sources or such as the directing agent or any pH adjustment agents which may be used.

One of the sources of silicon oxide, aluminum oxide or phosphorus oxide must initially be present in the organic phase of the reaction mixture. The aqueous phase will thus comprise the directing agent, cations and anions, pH adjustment agents and those sources of silicon oxide, phosphorus oxide and aluminum oxide which are not added to the organic phase.

The reaction mixture having the composition hereinbefore described is initially heated at a rate of 5°C to 200°C per hour up to a temperature of 80°C to 200°C and maintained within that temperature range until nucleation of SAPO-37 occurs. Then the reaction mixture is further heated at a rate of 5°C to 200°C per hour to a final temperature of 100°C to 300°C until crystals of desired SAPO-37 form, usually from 5 hours to 500 hours. The pH of the reaction mixture during crystallization is carefully maintained at from about 2 to about 9. This may be accomplished by adjusting the concentration of the added base(s).

During the heat-up and crystallization steps, the reaction mixture is agitated in a manner to intimately admix the substantially immiscible organic and aqueous phases. Techniques for dispersing the organic and aqueous phases in each other are well known in the art. It may even be desirable to form an emulsion of the organic and aqueous phases in order to maximize the interface between these liquid phases.

Following crystallization of the desired material, the reaction mixture containing same is filtered and the recovered crystals are washed, for example with water, and then dried, such as by heating at from 25°C to 150°C at atmospheric pressure.

In a more specific illustration of the present synthesis method, the aqueous phase contains the phosphorus and aluminum reagents, for example phosphoric acid and alumina. The organic phase with hexanol, for example, as solvent contains the silicon source, e.g. tetra-orthoalkylsilicate. The organic directing agent, i.e. a 37/1 mixture of tetrapropylammonium and tetramethylammonium cations, also acts as a surfactant to emulsify the aqueous and organic phases and optimize the interface. Silicon is progressively supplied during synthesis to the gel by hydrolysis of its organic compound and transfer of the product through the interface into the aqueous phase.

As silicon, aluminum and phosphorus must be available simultaneously to nucleate and crystallize the silicoaluminophosphate, the rates of supply of all three elements have to be comparable. This implies that the neutralization reaction, e.g. between H_3PO_4 and Al_2O_3 , and the hydrolysis of the organic silicon compound have to be concerted. Therefore, it may be important to predigest the alumina - phosphoric acid mixture. Even more critical will be the silicon supply rate which depends on factors such as the magnitude of the interface, temperature, pH of the aqueous phase, concentration, and nature of the organic solvent and of the silicon reagent.

Because the hydrolysis and transfer rates of silicon are controlled by the magnitude of the interface, as discussed earlier, silicon incorporation is expected to be favored as mixing increases.

pH is an important synthesis variable and as the formation of the silicoaluminophosphate proceeds, pH values of around or above neutral (i.e. 6 to 9) should be maintained. As the base stability of silicoaluminophosphate is expected to be intermediate between those of aluminum phosphates and zeolites, pH values of about or slightly above 8 are preferred. Because of the major role played by the hydrolysis of the silicon reagent and the necessity to control it in

the present method, there is a need to have a nearly constant pH during crystallization (in particular, to avoid rapid acid hydrolysis of the silicon source). This can be achieved by predigestion of alumina in phosphoric acid before addition of the other reagents, which raises the initial pH to 5-7.

To achieve and maintain higher pH values (pH = 8 or above), even after partial decomposition of the organic hydroxide, inorganic bases may be added.

The SAPO-37 prepared by the present method is beneficially subjected to thermal treatment to remove the organic directing agent. This thermal treatment is generally performed by heating at a temperature of 300°C - 100°C for at least 1 minute and generally not longer than 20 hours. While subatmospheric pressure can be employed for the thermal treatment, atmospheric pressure is desired for reasons of convenience. The thermally treated product is particularly useful in the catalysis of certain hydrocarbon conversion reactions.

The SAPO-37 synthesized hereby can be used as catalyst in intimate combination with a metal component such as silver, tungsten, vanadium, molybdenum, rhenium, chromium, manganese, or a Group VIII metal such as platinum or palladium where, for example, a hydrogenation-dehydrogenation or oxidation function is to be performed. Such a component can be ion-exchanged into the composition, impregnated therein or intimately physically admixed therewith. Such component can be impregnated into or onto the composition, such as, for example, in the case of platinum, by treating the crystal with a solution containing a platinum metal-containing ion. Thus, suitable platinum compounds include chloroplatinic acid, platinumous chloride and various compounds containing the platinum-amine complex.

The original ions, i.e. cations or anions, of the as synthesized SAPO-37 can be replaced in accordance with techniques well known in the art, at least in part, by ion exchange with other cations or anions. Preferred replacing cations include metal ions, hydrogen ions, hydrogen precursor, e.g. ammonium, ions and mixtures thereof. Particularly preferred cations include hydrogen, rare earth metals and metals of Groups IIA, IIIA, IVA, IB, IIB, IIIB, IVB, VIB and VIII of the Periodic Table of the Elements.

A typical ion exchange technique would be to contact the synthetic crystalline SAPO-37 with a salt of the desired replacing ion or ions. Examples of such salts of cations include the halides, e.g. chlorides, nitrates and sulfates.

Further, the present SAPO-37, when employed either as an adsorbent, ion-exchanger or as a catalyst in an organic compound conversion process should be dehydrated, at least partially. This can be done by heating to a temperature in the range of 200°C to 600°C in air or an inert atmosphere, such as nitrogen, etc. and at atmospheric, subatmospheric or superatmospheric pressures for between 30 minutes and 48 hours. Dehydration can also be performed at room temperature merely by placing the crystalline material in a vacuum, but a longer time is required to obtain a sufficient amount of dehydration. Therefore, depending upon the degree of dehydration or thermal treatment desired for the SAPO-37, it may be subjected to heating at a temperature of from 200°C to 1000°C for a time of from 1 minute to 48 hours.

The crystals of SAPO-37 prepared by the instant invention can be shaped into a wide variety of particle sizes. Generally speaking, the particles can be in the form of a powder, a granule, or a molded product, such as an extrudate having a particle size sufficient to pass through a 2

mesh (Tyler) screen and be retained on a 400 mesh (Tyler) screen. In cases where the composition is molded, such as by extrusion, the crystals can be extruded before drying or partially dried and then extruded.

In the case of many catalysts, it is desired to incorporate the SAPO-37 with another material resistant to the temperatures and other condition employed in organic conversion processes. Such materials include active and inactive material and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Use of a material in conjunction with the SAPO-37, i.e. combined therewith, which is active, tends to improve the conversion and/or selectivity of the catalyst in certain organic conversion processes. Inactive materials suitably serve as diluents to control the amount of conversion in a given process so that products can be obtained economically without employing other means for controlling the rate of reaction. These materials may be incorporated into naturally occurring clays, e.g. bentonite and kaolin, to improve the crush strength of the catalyst under commercial operating conditions. Said materials, i.e. clays, oxides, etc., function as binders for the catalyst. It is desirable to provide a catalyst having good crush strength because in commercial use it is desirable to prevent the catalyst from breaking down into powder-like materials. These clay binders have been employed normally only for the purpose of improving the crush strength of the catalyst.

Naturally occurring clays which can be composited with the new crystal include the montmorillonite and kaolin families which include the subbentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anaxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification. Binders useful for compositing with the present crystal also include inorganic oxides, notably alumina or silica.

In addition to the foregoing materials, the SAPO-37 produced can be composited with a porous matrix material such as aluminum phosphate, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silicitanita as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The relative proportions of finely divided crystalline SAPO-37 material and inorganic oxide gel matrix vary widely, with the crystal content ranging from 1 to 90 percent by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of 2 to 80 weight percent of the composite.

The crystalline material produced by the present process is readily convertible to catalytically active material for a variety of organic, e.g. hydrocarbon, compound conversion processes. Such conversion processes cracking hydrocarbons with reaction conditions including a temperature of from 300°C to 700°C, a pressure of from 10 to 3040 kPa (0.1 to 30 atmospheres) and a weight hourly space velocity of from 0.1 to 20 hr⁻¹; hydrocracking hydrocarbons when the catalyst is associated with an appropriate hydrogenation metal, e.g., noble metal, cobalt, and molybdenum with reaction conditions including a temperature of from 300°C to 450°C, a hydrogen pressure of from 6585 to 20285 kPa (65 to 200 atmospheres) and a weight hourly space velocity of from 0.5 hr⁻¹ to 5 hr⁻¹; and isomerizing xylene feedstock components with reaction conditions in-

cluding a temperature of from 230°C to 510°C, a pressure of from 304 to 3546 kPa (3 to 35 atmospheres), a weight hourly space velocity of from 0.1 to 200 and a hydrogen/hydrocarbon mole ratio of from 0 (e.g. 0.1) to 100.

In general, therefore, catalytic conversion conditions over a catalyst comprising SAPO-37 in active form include a temperature of 230°C to 700°C, a pressure of from 10 to 20265 kPa (0.1 to 200 atmospheres), a weight hourly space velocity of from 0.1 hr⁻¹ to 200 hr⁻¹ and a hydrogen/organic, e.g. hydrocarbon, compound of from 0 to 100.

The crystalline material of the present invention is also useful for sorptive separation of para- and meta-xylene isomers when the crystal is associated with large cations, such as, for example cesium or alkaline earths, e.g., barium or calcium.

In order to more fully illustrate the nature of the invention and the manner of practicing same, the following examples are presented.

When Alpha Value is examined, it is noted that the Alpha Value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst and gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time). It is based on the activity of the highly active silica-alumina cracking catalyst taken as an Alpha of 1 (Rate Constant = 0.015 sec⁻¹). In the case of zeolite HZSM-5, only 174 ppm of tetrahedrally coordinated Al₂O₃ are required to provide an Alpha Value of 1. The Alpha Test is described in U.S. Patent 3,3543,078 and in The Journal of Catalysis, Vol. IV, pp. 522-529 (August 1965).

When ion-exchange capacity is examined, it is determined by titrating with a solution of sulfamic acid the gaseous ammonia evolved during the temperature programmed decomposition of the ammonium-form of the crystalline material. The method is described in Thermochemica Acta, Vol. III, pp. 113-124, 1971 by G.T. Kerr and A.W. Chester.

EXAMPLE 1 (COMPARATIVE)

In this example, SAPO-37 was prepared as in Example 43 of U.S. Patent 4,440,871.

A reaction mixture was prepared by stirring 30.5 g water, 27.7 g H₃PO₄ (85%), and 16.6 g Al₂O₃ (Catapal from Conoco) until homogeneous. To this mixture was added a dispersion of 3.1 g silica (HiSil) in 116 g TPAOH 40% (tetrapropylammonium hydroxide) and 1.1 g TMAOHx5H₂O (solid tetramethylammonium hydroxide). This reaction mixture contained from 1.3 to 1.5 grams of available silicon. The reaction mixture was stirred until homogeneous and placed into a 300 ml stainless steel autoclave and heated to 200°C for 24 hours with moderate stirring. The pH of the mixture was 8.5. The solid product was filtered, washed with water and dried. The yield of as-synthesized material was 9.7 g. The product had an X-ray diffraction pattern typical of materials having the faujasite type structure as shown in Table II. The product was submitted for chemical analysis and the results gave the following composition in weight %:

Silicon	5.07 wt %
Aluminum	15.13 wt %
Phosphorus	13.31 wt %

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TABLE II

d-space	2xtheta	I/I ₀
14.336	6.160	100
8.771	10.077	28
7.479	11.824	9
7.159	12.354	3

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5.687	15.569	73
4.769	18.595	60
4.379	20.264	26
4.186	21.207	6
3.915	22.691	21
3.777	23.537	66
3.467	25.675	10
3.308	26.928	45
3.222	27.665	3
3.024	29.510	11
2.917	30.622	15
2.858	31.268	30
2.768	32.320	7
2.639	33.941	12
2.595	34.535	4

EXAMPLE 2 (COMPARATIVE)

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The synthesis of Example 1 was repeated and yielded 9.5 g of a solid dry product with an X-ray diffraction pattern identical to the one of the Example 1 product. The composition of the product was:

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Silicon	3.60 wt %
Aluminum	17.27 wt %
Phosphorus	12.46 wt %

EXAMPLE 3 (COMPARATIVE)

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Fractions of the products of Examples 1 and 2 were examined under a light microscope (Nikon, total enlargement 400 x). The crystals in either batch were octahedra with fully developed crystal faces or intergrowths of cubic crystals. Their size was 2 to 10 microns.

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EXAMPLE 4 (COMPARATIVE)

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A fraction of the solid product of Example 1 was calcined as described in U.S. Patent 4,440,871, Example 43, and exchanged in a solution of 1 M NH_4Cl . The product of this exchange was heated in helium in a TGA furnace to 1000°C and the evolved NH_3 was titrated. The amount of titrant needed was 0.29 meq/g of ash.

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EXAMPLE 5

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In this example, SAPO-37 was prepared by the present invention.

A two-phase reaction mixture was prepared comprising an aqueous and an organic phase. The organic phase was immiscible with the aqueous phase. In order to make this Example comparable to Examples 1 and 2 above, the molar concentrations of the main constituents (Si, Al, P, and the directing agents) were kept constant. Hence, an aqueous phase containing 30.5 g water, 27.7 g H_3PO_4 (85%), and 16.6 g Al_2O_3 (Catapal from Conoco) was prepared and stirred until homogeneous. As directing agent a mixture of 116 g TPAOH (40 wt % in water) and 1.1 g $\text{TMAOH} \cdot 5\text{H}_2\text{O}$ (solid crystals) were added to this mixture and dissolved. The mixture was digested for 1 hour at 80°C. An organic phase was prepared by mixing 60 g 1-hexanol and 10.7 g $\text{Si}(\text{OC}_2\text{H}_5)_4$. The two phase reaction mixture had from 1.4 to 1.5 grams of available silicon. The two phases were added together in a beaker and stirred; then the reaction mixture was transferred into a 300 ml steel autoclave. The mixture was heated at a rate of 50°C per hour to 130°C with stirring (800 rpm) for 24 hours and then kept at 200°C for 24 hours. The pH was maintained at 9.0. The solid product was filtered, washed with water and dried. The yield of as-synthesized material was 23 g. The product had an X-ray diffraction pattern typical of materials having the faujasite type structure as shown in

Table III. Occasional small amounts of impurities were found in the product (marked with an asterisk in the Table). The product was submitted for chemical analysis and the results gave the following composition in weight %:

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Silicon 4.38 wt %
 Aluminum 17.95 wt %
 Phosphorus 11.53 wt %

TABLE III

<u>d-space</u>	<u>2xtheta</u>	<u>I/I₀</u>
14.345	6.156	100
11.981	7.372*	10
8.767	10.081	32
7.479	11.824	8
7.149	12.371	4
5.981	14.799*	4
5.683	15.580	72

TABLE III (cont.)

<u>d-space</u>	<u>2xtheta</u>	<u>I/I₀</u>
4.846	18.291*	8
4.766	18.602	64
4.520	19.625*	9
4.376	20.279	28
4.239	20.941*	7
4.186	21.208	5
3.987	22.282*	8
3.913	22.704	18
3.775	23.550	62
3.463	25.704	12
3.307	26.940	46
3.225	27.630	4
3.021	29.541	8
2.915	30.641	16
2.856	31.289	31
2.767	32.330	8
2.637	33.974	10
2.596	34.517	2

EXAMPLE 6

The synthesis of Example 5 was repeated and yielded 25 g of a solid dry product with an X-ray diffraction pattern identical to the one of the Example 5 product. The composition of this product was:

Silicon	3.74 wt %
Aluminum	17.04 wt %
Phosphorus	14.00 wt %

EXAMPLE 7

Fractions of the solid products of Examples 5 and 6 were examined by light and scanning electron microscopy. The crystals were small (below 0.5 microns) and agglomerated. The small crystal size can be related to the broadened X-ray diffraction lines obtained from the products.

EXAMPLE 8

A fraction of the solid product of Example 5 was treated by heating it to 450°C in nitrogen and keeping it at that temperature for 4 hours, then exchanging it in a solution of 1 M NH_4Cl . A fraction of the product of this exchange was heated in helium in a TGA furnace to 1000°C and the evolved NH_3 was titrated. The amount of titrant needed was 1.02 meq/g of ash.

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EXAMPLE 9

A fraction of the exchanged product of Example 8 was tested in the Alpha Test. The Alpha Value was found to be 1.0.

EXAMPLE 10

The synthesis of Example 5 was again repeated, except that the temperature was raised to 200°C directly at 50°C/hour and kept there for 48 hours. The crystalline product had the diffraction pattern of material having the ALPO-5 structure type (U.S. Patent 4,310,440), and being indistinguishable from SAPO-5 (U.S. Patent 4,440,871).

The above examples illustrate the improvement of the present invention. The following tabulation clarifies the comparison. Cation exchange sites as a measure of titrant needed in TGA is indicated.

TABLE IV

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<u>Examples</u>	<u>Synthesis Reaction Mixture Silicon Available, g</u>	<u>Product</u>	<u>Product Silicon Wt. %</u>
1,4	1.3-1.5	SAPO-37	5.07
2	1.3-1.5	SAPO-37	3.60
5,8	1.4-1.5	Improved SAPO-37	4.38
6	1.4-1.5	Improved SAPO-37	3.74

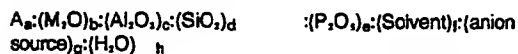
<u>Examples</u>	<u>Yield of, SAPO-37, g</u>	<u>Product Silicon, g</u>	<u>Titrant Needed</u>
1,4	9.7	0.49	0.29 meq/gram
2	9.5	0.34	--
5,8	23.0	1.01	1.02 meq/gram
6	25.0	0.94	--

When the present method is not followed, such as when the temperature increasing step is not followed, SAPO-37 is not obtained, as illustrated in Example 10.

Claims

1. A method for synthesizing a crystalline material comprising silicon, phosphorus and aluminum and exhibiting a characteristic X-ray diffraction pattern as shown in Table I of the specification which comprises:

a) preparing a reaction mixture comprising a liquid organic phase and a liquid aqueous phase, said reaction mixture comprising water, sources of aluminum oxide, silicon oxide, phosphorus oxide, an organic directing agent A, inorganic cations M and anions, and a substantially water-immiscible organic solvent, the components of said reaction mixture having the following relationship:



wherein a, b, c, d, e, f, g and h are numbers satisfying the following relationship:

$a/(c+d+e)$ is less than 4,

$b/(c+d+e)$ is less than 2

$d/(c+e)$ is less than 2,

$f/(c+d+e)$ is from 0.1 to 15,

$g/(c+d+e)$ is less than 2, and

$h/(c+d+e)$ is from 3 to 150,

wherein upon initial preparation of said reaction mixture the source of one of the aluminium, silicon or phosphorus oxides is dispersed or dissolved in said organic phase;

b) heating said reaction mixture at a rate of from 5°C to 200°C per hour to a temperature of from 80°C to 200°C;

c) agitating said reaction mixture in a manner sufficient to intimately admix said liquid organic and aqueous phases with each other;

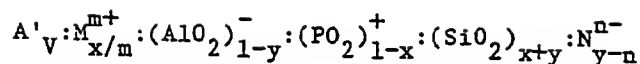
d) when nucleation of said crystalline material occurs, heating said agitated reaction mixture at a rate of from 5°C to 200°C per hour to a temperature of from 100°C to 300°C;

e) maintaining said agitated reaction mixture at a temperature of from 100°C to 300°C and a pH of from 2 to 9 until crystals of said crystalline material are formed; and

f) recovering from said reaction mixture said crystalline material characterized by a composition, in the anhydrous state, as follows:

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wherein A' represents the total of organic directing agent A plus organic solvent, v is the number of moles of A', m is the valence of cation M, n is the valence of anion N, and x and y are numbers of from greater than -1 to less than +1 which satisfy the relationship:

(1) if x is 0, then y is not 0,

(2) if y is 0, then x is not 0,

(3) the sum of x + y is greater than 0 and less than 1,

said crystalline material having an ion exchange capacity of at least about 0.05 meq/g.

2. The method according to Claim 1 wherein said organic

directing agent A is a mixture of tetrapropylammonium and tetramethylammonium compounds.

10 3. The method of Claim 1 or Claim 2 wherein the source of silicon oxide is initially present in the organic phase of the reaction mixture and wherein the pH of the agitated reaction mixture is maintained between 6 and 9.

15 4. The method of anyone of Claims 1 to 3 which comprises the additional step of heating the recovered crystalline material at a temperature of from 300°C to 1000°C.

20 5. A process for converting an organic compound which comprises contacting said organic compound at conversion conditions with a catalyst comprising the synthetic crystalline material produced by the method of Claim 4.

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Synthesis of a crystalline silicoaluminophosphate.

A method for the synthesis of the silicoaluminophosphate SAPO-37 comprises preparing a two-phase reaction mixture containing the required starting materials divided between a liquid organic phase and a liquid aqueous phase. The reaction mixture is then heated at a rate of from 5°C to 200°C per hour to a temperature of from 80°C to 200°C, while being agitated in a manner sufficient to intimately admix the liquid organic and aqueous phases. Once nucleation of the silicoaluminophosphate occurs the agitated reaction mixture is heated at rate of from 5°C to 200°C per hour to a temperature of from 100°C to 300°C and maintained then at the higher temperature and at a pH of from 2 to 9 until crystals of the desired silicoaluminophosphate are formed.

EP 0 185 525 A3



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 85 30 9095

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
P, X	EP-A-0 147 991 (MOBIL OIL) * claim 7 *	1, 3	C 01 B 33/28
A	* examples 9, 11, 14, 16 *	2, 3	
A	EP-A-0 103 117 (UNION CARBIDE) * page 8, line 12 - page 15, line 26 * & US - A - 44 40871 (Cat. D)	1	
A	DE-A-2 041 377 (UNION CARBIDE) * claim 3 *	1	
A	DE-A-2 037 511 (UNION CARBIDE) * claims 3, 4 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 01 B 33/28
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 19-12-1988	Examiner CLEMENT J.P.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document; but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			